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Measurement and control of reagent concentrations in MOCVD reactor using ultrasonics

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An ultrasonic cell for monitoring gas mixtures on MOCVD reactors has been developed from being a laboratory instrument to a standard, rack-mounted, system which interacts with the reactor's computer, and is marketed under the trade name of EPISON. A feedback circuit has been implemented to stabilize the TMI mole fraction in the reactor. The effectiveness of the feedback circuit has been tested by growing InGaAs layers, during which the TMI concentration was deliberately perturbed by changing the pressure of the TMI line. Using feedback correction an X-ray rocking-curve peak with a FWHM of 25 arc sec was obtained for a layer grown with the same perturbations which had previously led to a 400 arc sec FWHM without feedback.

1. Introduction

A particular difficulty arises from using trimethylindium (TMI) as a group III source in MOCVD of III–V compound semiconductors. A lack of reproducibility in obtaining lattice-match of alloys grown with TMI indicates that the pick-up efficiency of TMI sources is often not reproducible [1,2]. The usual assumption made, that the flow of a carrier-gas through a source results in saturation of the carrier-gas by the vapour of the source, is not necessarily valid for TMI which, as a solid, has a limited surface area exposed to the carrier gas. The use of TMI source temperatures at or below room temperature necessitates relatively large carrier gas flows due to the low vapour pressure of TMI. This further reduces the likelihood of achieving saturation of the carrier gas. The distribution of solid TMI within the source bottle, and hence the degree of saturation of carrier gas depends on the life history of the source [1]. This distribution can affect the pick-up efficiency, which cannot be accurately measured using conventional instruments such as flow regulators.

Initially an experimental ultrasonic system was designed and constructed, which has been shown to measure TMI concentrations on MOCVD reactors very accurately [3–5]. The system comprises various electronic units which control a stainless steel chamber, or ultrasonic cell, through which passes the gas mixture to be analysed. The chamber contains two ultrasonic transducers at either end of an internal volume and separated by an accurately known distance. The time for acoustic pulses to travel between the transducers is measured by electronic timing techniques. High precision in the timing of the pulses is achieved by ensuring that the pulse trigger times are not affected by changes in signal height due to acoustic standing waves in the chamber. The temperature of the gas is measured by a platinum resistance thermometer. The gas concentration in a binary mixture such as TMI and hydrogen may be calculated by combining the values of temperature and acoustic velocity. The particular features of this system are the high precision of the measurement, equivalent to $\pm 0.001\%$ in TMI concentration in hydrogen, and also the high purity of the components and rigorous hermetic seal which permit carrier concentrations as small as 3×10^{14} cm^{-3} in undoped InP epilayers [6]. The system has now been further developed as a commercial product, the EPISON [7]. This paper

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describes the improvements and use of the EPISON to measure and control the TMI molar flow rate into a low-pressure MOCVD reactor.

2. Instrument changes

The ultrasonic cell remains unchanged, but the electronic control circuitry has been redesigned and much reduced in size. The electronics are now contained in a standard rack-mounted module. Signal-to-noise has been improved by siting the signal preamplifier integrally with the ultrasonic cell module.This enables measurements to be made, with the precision given above, but at 1 s intervals compared with 60 s intervals in the original laboratory instrument. The EPISON can be used as a self-contained unit which provides direct readout of concentration for any binary mixture by simply defining the two gases in terms of their physical constants. The binary mixture flows through the chamber at any pressure between 400 and 1200 mbar. Alternatively, and as reported here, the EPISON is simply interfaced with the computer which routinely controls the reactor gas handling system. The measured concentration can be read by the computer which then modifies the flow through the TMI to maintain a constant TMI molar flow rate, i.e., the product of measured concentration and flow is maintained constant.

3. Discussion

The long-term behaviour of the pick-up efficiency of TMI sources is typically similar to that shown in fig. 1. The vapour pressure decreases with usage of the source. This makes it difficult to maintain accurate lattice-match of InGaAs, e.g. to within 50 ppm, over a period of several growth runs. For comparison, the vertical bar in fig. 1 shows a change in TMI vapour pressure equivalent to a lattice-match change of 400 ppm, calculated for InGaAs grown with a constant gallium content. It is evident that changes of this size can occur over periods of about ten growth runs. In principle it should be possible to compensate for run-to-run changes in TMI concentration, as measured at the start of a growth run, by making a single appropriate change in the volume flow rate of hydrogen. This would be straightforward provided the TMI concentration was independent of the hydrogen flow. In practice this is not the case.

Fig. 2 shows the variation of TMI concentration with hydrogen flow. Not only does the TMI concentration vary with hydrogen flow, but it does so in an unpredictable manner. The data

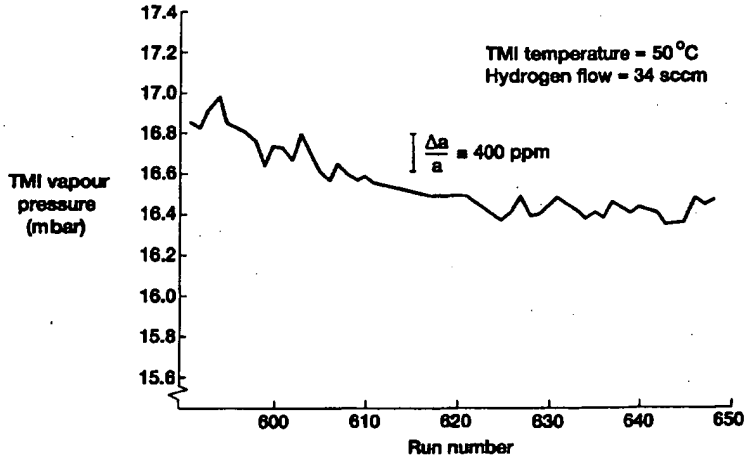

Fig. 1. Vapour pressure of a TMI source against run number. The hydrogen flow was 34 SCCM.

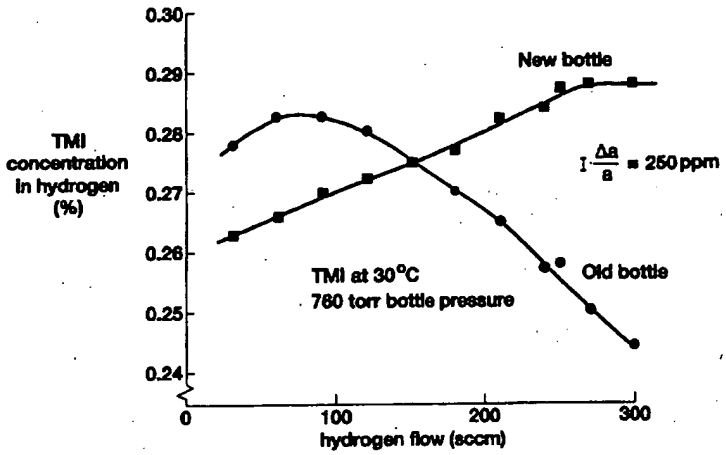

Fig. 2. Variation of TMI concentration with hydrogen flow.

were acquired on two TMI sources installed on a low pressure MOCVD reactor, and correspond to measurements for 10 min periods at each different flow rate. It is apparent that undesirable changes equivalent to lattice-mismatch changes of 250 ppm can occur when the flow rate is deliberately changed, or even during a 10 min growth at a constant flow rate. The stability of TMI concentration generally improves after the first 10 min at a given hydrogen flow rate, but it is not possible to predict the stability either for the duration of a growth run or from one run to the next. The detailed behaviour of the TMI vapour pressure seems to depend on the history of the TMI source.

4. Experimental procedure

To compensate for variations in TMI pick-up efficiency, the hydrogen mass flow controller on the TMI line is adjusted continually via the reactor computer so as to maintain a constant TMI molar flow rate. For growth runs lasting several hours, the hydrogen is set to flow through the TMI source to the vent for 20 min to allow the vapour pressure to stabilize. Then the feedback loop is closed and the growth run commences.

The effectiveness of the feedback system was investigated by examining the homogeneity of InGaAs layers grown both with and without EPISON feedback under conditions which deliberately simulated an unstable TMI source. In the first experiment the total gas pressure in the TMI line was changed in abrupt, discrete steps, each being maintained for 10 min, to give, ideally, a total of four distinct TMI concentrations. The pressures used were 619, 655, 680 and 717 Torr. The hydrogen flow rate was held constant at 276 SCCM, and a feedback loop time-constant of 10 s was found to be suitable at this flow-rate. The changes in total pressure were made by programming an MKS pressure control valve in the TMI line via the control computer. The corresponding steady-state TMI concentrations were approximately 0.329, 0.312, 0.303 and 0.289%, and were reached shortly after the abrupt changes in pressure. The finite time to change concentrations occurs because, although the TMI concentration in the TMI bottle changes abruptly, the mixture in the ultrasonic cell remains at the original concentration until it is replaced by a new mixture from the TMI bottle. It took about 20 s to change completely from the original concentration to the new concentration with the flow-rate used above. The InGaAs growths were started after an initial 60 min period during which hydrogen flowed through the TMI source, either to vent or through the reactor to grow an InP buffer-layer, to stabilize the TMI vapour pressure at this flow-rate. It should be noted that these pressure changes of

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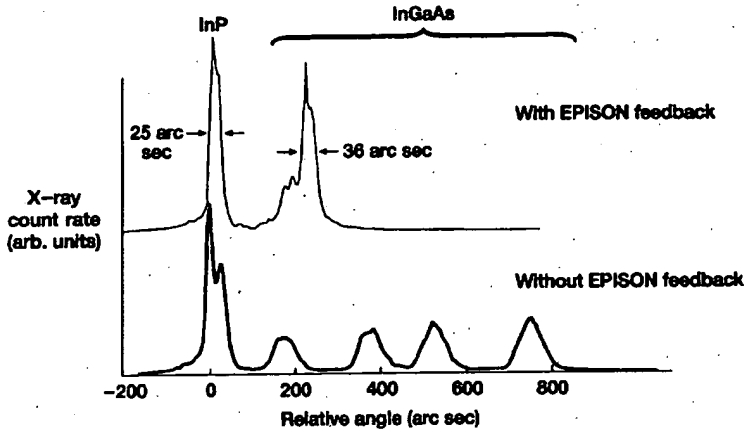

Fig. 3. X-ray rocking curves for InGaAs epilayers grown whilst the total pressure in the TMI source was stepped at 619, 655, 680 and 717 Torr.

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the TMI sources did not alter the MOCVD reactor pressure which was held constant at 150 Torr.

Fig. 3 shows double crystal X-ray measurements of the layers grown, on a (100) InP substrate, with and without the feedback loop operative. With no feedback there are four distinct peaks corresponding to four different InGaAs compositions and covering a range on the X-ray measurement of about 600 arc sec. With feedback the composition was controlled to a range of about 100 arc sec: the peaks now overlap, giving an overall FWHM of 36 arc sec. It should be noted that these large, rapid, changes in TMI concentration were extreme conditions for the feedback system to compensate for and are unlikely to occur under normal circumstances. The degree of control achieved is nevertheless very good.

A second experiment was then done in which the same four distinct pressures were applied for 10 min periods, but the changes in pressure were made by linearly ramping over 200 s. The X-ray

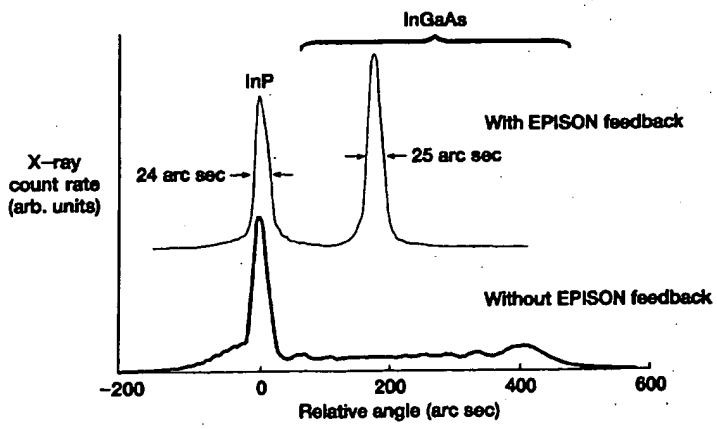

Fig. 4. X-ray rocking curves for InGaAs epilayers grown whilst the total pressure in the TMI source was linearly ramped from 770 to 868 Torr.

rocking curve on the sample grown with EPISON feedback now shows a range of composition corresponding to about 80 arc sec but with a single peak of 36 arc sec FWHM, i.e., slightly better stabilization than in the first experiment has been obtained. Nevertheless, the FHWM is larger than is desirable and represents a small residual lack of control of the composition.

Finally a third experiment was done in which the pressure was linearly ramped throughout the InGaAs growth from 770 to 868 Torr over a 40 min period. Fig. 4 shows that, when no feedback was used, the InGaAs gives a diffuse, very broad X-ray signal, of about 400 arc sec width. When EPISON feedback was used, a single narrow peak of 25 arc sec FWHM was obtained, possibly limited by substrate bowing. The conditions were the most realistic of the three experiments, since naturally occurring changes in TMI vapour pressure also are slow and gradual [1,3,4]. The result demonstrates the high degree of control over the TMI flow that may be obtained using the EPISON feedback system on slowly changing pressures.

5. Conclusions

An ultrasonic system for monitoring the concentration of gas mixtures on MOCVD reactors has been developed from being a large and complex laboratory prototype to a compact, user-friendly, commercially manufactured system, and is manufactured under the trade name of EPISON. InGaAs layers grown using a feedback circuit from the EPISON to stabilize the TMI molar flow rate, during growth runs in which changes were deliberately induced, have shown that the technique is extremely effective in compensating for gradual changes in TMI concentration. The feedback technique may also be applied to stabilize the run-to-run composition of InGaAs and InGaAsP alloys, thereby avoiding long term drift as the sources age.

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Applications in the study of the reacti as alternativ

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1. Introduction

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